

NMR Based Investigation of the Effects of Aging on the Motional Properties of Cellular Silicone Foams

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NMR Based Investigations of the Effects of Aging on the Motional Properties of Cellular Silicone Foams

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Introduction

The aging of polymeric composite materials, such as filled polydimethylsiloxane foams, through factors such as thermal and mechanical stresses, environment, radiation, and chemical attack can affect the length of time for which a given material can maintain its engineering performance. Iterative interactions and cumulative reactions may result in the material or device reaching a critical age where its properties fail unexpectedly and catastrophically. The mechanical property changes associated with multi-mechanism aging may be subtle, and may not necessarily change linearly as a function of time in service. Since such linear relationships are often used in lifetime predictions, there is a fundamental need to develop and employ spectroscopic methods to investigate the structural and motional changes that occur in these organic-inorganic materials as a result of aging in chemically, thermally, or radioactively harsh environments.

We have used multinuclear nuclear magnetic resonance (NMR) spectroscopy to characterize aging signatures in a series of PDMS based composite materials. Unfortunately, ^{13}C , ^{29}Si , and ^1H magic angle spinning NMR spectra remain unchanged with gamma radiation exposure up to 50Mrad. This suggests that the speciation related changes are small and occur at a frequency of less than approximately 1% of the monomer units. As a result, we have shifted focus and have employed relaxation studies to monitor changes in motional properties of the copolymer foams caused by irradiation. We have measured spin-lattice, spin-spin, and rotating frame spin-lattice relaxation times for PDMS model rubbers with variable cross link density and filler content, for M9760 foams irradiated from 0 to 50Mrad, and for dehydrated M9760 foams. Spin-lattice relaxation times, in general, are sensitive to fast molecular motions in the MHz frequency range. Spin-spin and rotating frame relaxation times, on the other hand, are sensitive to changes in slower motion processes in the kHz range [1]. Comparison of changes in these relaxation parameters in the irradiated samples to mechanical properties, cross-link density, and filler content dependencies observed in the model compounds have lead to a picture of the changes in motional properties of the foam due to irradiation and water content. The characterization of motional changes in the foams could provide important data for predictive modeling efforts. In addition, we have also developed empirical relationships between relaxation times and interfacial and bulk polymer motional properties that might allow rapid NMR based screening methods to compliment solvent swelling experiments.

Experimental

The materials tested were a copolymer of polydimethylsiloxane and polydiphenylsiloxane, crosslinked by a vinyl monomer/vinyl-specific catalyst system. The percentages of each monomer unit in the base rubber were 90.7% PDMS, 9.0% PDPS, and 0.31% polymethylvinylsiloxane. This rubber was then milled with a mixture of fumed and precipitated filler (21.6 and 4.0 wt%, respectively), and 6.8 wt% of an ethoxy end-blocked siloxane added as a processing aid. The composite was studied in foamed form made by processing the filled polymer with prilled urea, which is subsequently washed out. M9750 and M9760 are the designations for the porous filled polymer foams, exhibiting 50 and 60 percent porosity respectively. Samples were irradiated in a stainless steel container ($V \sim 2$ liters) that was exposed to a Co^{60} source

(0.5Mrad/hr) for various periods of time. Vacuum samples were encapsulated in glass tubes (20 minutes pump time, 1 mtorr), while air irradiated samples were left open to the air environment inside the container. All experiments were performed at the same dose rate.

The following surveillance return samples were also studied: S255546 s/n's 1163, 1692, 1358, 1197, S255541 s/n's 1339, 1091, 1237, 1626, S545505 s/n's 2041, S545506 s/n's 2081, 1893, 1181, and S545507 s/n's 2834, -2679, 1286.

¹H T₂ measurements and ¹H DQ 2D NMR measurements were performed at 500.13MHz on a Bruker DRX-500 spectrometer using a HCX 5mm probe. ¹H Excitation pulses of 7μs and relaxation delays of 10 seconds were used. In all cases, small (0.5cm x 0.5cm) squares of foam were cut from the larger foam and set in the portion of a 5mm NMR tube that would be within the coil volume of the probe. T₂'s were determined by fitting the decay of Hahn spin-echo intensity with echo delay time as detailed previously, to a double exponential decay. Errors in T₂ values were estimated from analysis of 4 replicate runs for 3 different samples. For the replicate runs, separate samples of the foams were cut from the samples provided. DQ experiments were performed with a standard 90-t-180-t₁-90-acquire (t₂) pulse sequence (8,13,14). The 2D time domain data set was processed in magnitude mode in t₂. DQ intensities were scaled for differences in sample mass and fits to the intensity versus DQ preparation time were performed by a non-linear least squares fit of the data. Q_{DC} experiments were performed by measuring the intensity of the stimulated echo for delays t₁ and t₂ (7,9) and the intensity of the primary echo for delay t₁. The ratio of the stimulated to the primary echo (A_{stim}/A_{prime}) is defined as the dipolar correlation coefficient (Q_{DC}). Experiments were performed at 299.995MHz in a field gradient of 2G/mm. Measurements of spin-echo intensity as a function of field gradient showed that this gradient strength was below the gradient where decay due to diffusion would occur. 90° pulse widths of 3.7μs were used with t₂=50ms. For the stimulated echo, a long decaying component due to free polymer chains was subtracted from the data before dividing by the intensity of the prime echo.

Results and Discussion

¹H spin-lattice relaxation times (T₁) were measured for all filled PDMS samples and remained constant within experimental error at 1.15±0.05 sec at ambient temperature. Though the ¹H T₁s of the present samples are lower than the T₁'s reported for low and high molecular weight PDMS linear polymers subjected to γ-irradiation and for unfilled model PDMS, the invariance of T₁ with irradiation is reproduced [2]. The invariance of the ¹H spin-lattice relaxation times to dose rates lower than 50Mrad is a consequence of the only relatively minor effects of any additional cross-linking and entanglements on the rapid motion of the methyl groups around the Si-C, C₃, axis.

Spin-echo decay curves, shown in figure 1 for irradiated foams, were in all cases, characterized by two relaxation times that dominated at short and long taus, respectively:

$$M(t) = X_s \exp(-\tau/2T_{2s}) + X_L \exp(-\tau/2T_{2L}) \quad \{1\}$$

where X_s and X_L represent the mole fractions of spins undergoing transverse relaxation with the short (T_{2s}) and long (T_{2L}) relaxation times. In agreement with Charlesby [2] and Cohen-Addad [3], we assign the two different relaxation times to protons in environments with a large degree of network structure (T_{2s}) and free, low molecular weight polymer chains (T_{2L}). The values for the relaxation times are plotted as a function of dose in air and in vacuum in figures 2. As the cumulative dose increased for samples irradiated in air, the transverse relaxation times first increased to a maximum of 0.56 ms at 5 Mrad and then decreased to 0.42 ms at 50 Mrad. For samples irradiated in vacuum, the T₂ steadily decreased with dose to 0.26 ms at 25 Mrad. The large differences in the two relaxation times reflect the large difference in molecular mobilities of the two regions of the polymer system.

Figure 1. ^1H Spin-echo NMR decay curves for γ -irradiated silica-filled silicone foams.

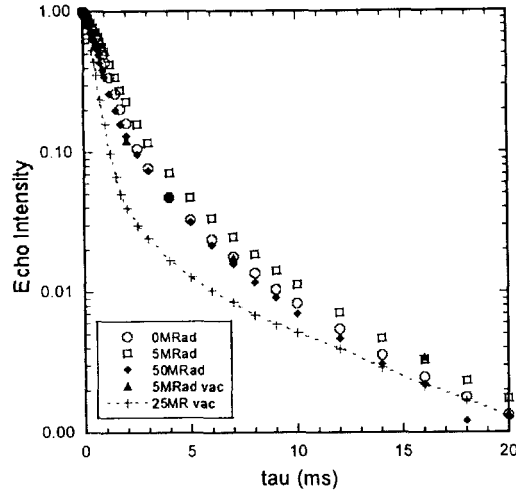
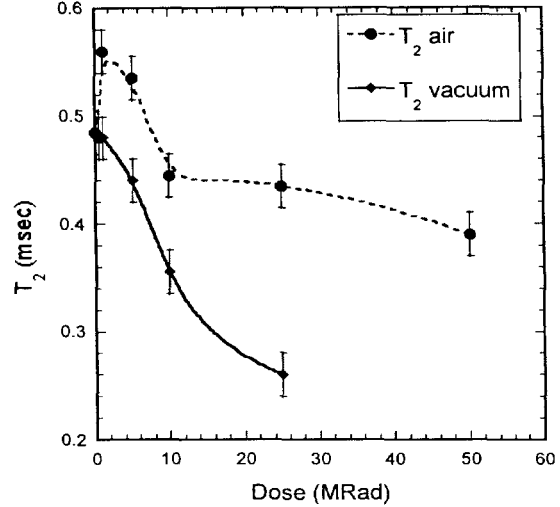


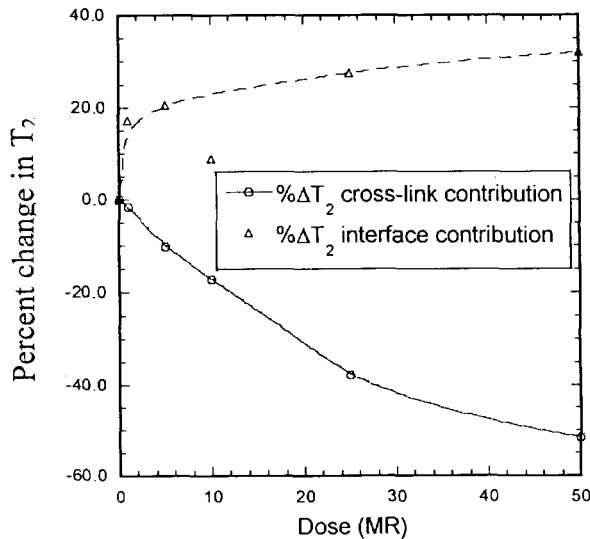
Figure 2. T_2 vs. dose for silica filled silicone polymer samples.



The experimental observations for samples irradiated in air are consistent with an initial structural relaxation of the lattice. This is due to either chain scission or a disruption of the hydrogen bonding between the polymer and silica filler. Since chain scission has not been found to be a significant contribution to γ -irradiation induced damage in linear PDMS polymers [2], the initial increase in T_{2s} is likely due to the latter explanation. At doses higher than 5MRad, the T_2 data suggests that the changes in the polymer morphology are characterized by a hardening of the lattice due to continued crosslinking of the polymer network. For samples irradiated in vacuum, no initial increase in T_{2s} was seen. This suggests that the mechanisms of morphological changes are dominated by cross-linking in the polymer network and/or at the polymer/silica interface.

In an effort to resolve changes spectroscopically in bulk polymer and interfacial crosslink density (CLD) interactions by rapid ^1H NMR analysis, we have combined the T_2 analysis with measurements of residual dipolar couplings by multiple quantum and dipolar correlation effect NMR spectroscopy [4,5]. Experimental observations have suggested that the residual dipolar couplings measured by these methods measure cross-link density changes in the bulk polymer only while T_2 measurements measure interfacial and bulk changes to cross-link density. Empirical relationships have been determined for the differing contributions to changes in T_2 due to polymer crosslinks and interfacial interactions:

Figure 3. Percent change in T_2 due to changes in CLD and interfacial interactions obtained from empirical correlations between T_2 and $\langle \delta\Omega_{\text{dred}}^2 \rangle$.



$$\Delta T_{2\text{poly}} = 0.33 * \Delta \langle \delta \Omega_{\text{dred}}^2 \rangle$$

(polymer cross link contribution)

$$\Delta T_{2\text{inter}} = [T_2(\text{XMR}) - T_2(0\text{MR})] - \Delta T_{2\text{poly}}$$

(interface contribution)

Figure 4. $T_{2\text{short}}$ as a function of age for SR samples.

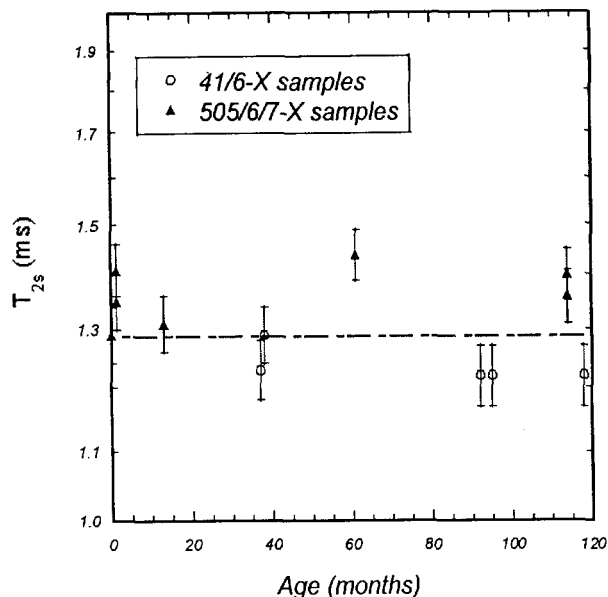
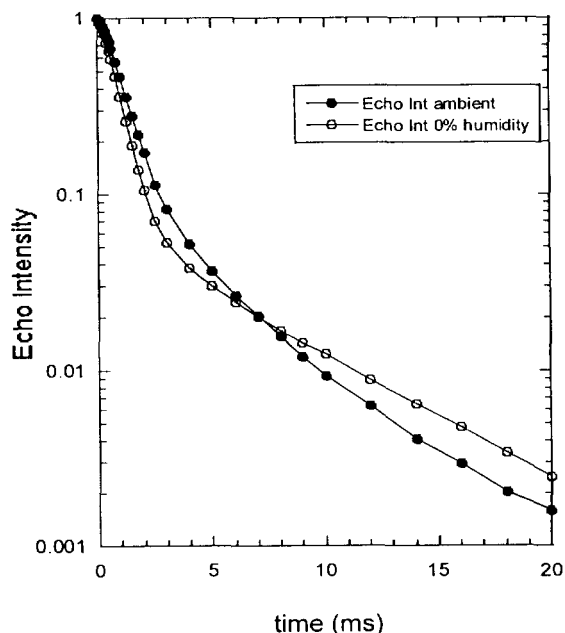


Figure 5. ^1H spin-echo decay curves for M9760 foam at ambient and 0% relative humidity.



increased. It is also possible that the decrease in T_{2s} reflects an increase in effective cross-link density due to more efficient hydrogen bonding to the silicone co-polymer brought about by dehydration of the silica surface. In light of these NMR results the influence of water on the

The separate contributions to T_2 due to polymer crosslinking and changes in interfacial bonding have been calculated for the γ -irradiated samples and are plotted in figure 3. The data shown in this figure are remarkably similar to data obtained by solvent swelling techniques and were acquired in only a few hours instead of a few weeks [6]. However, the above analysis is based on empirical correlations only and additional experiments should be performed to more firmly link the above correlation to fundamental physical and chemical parameters.

The results of the double exponential fits to the ^1H T_2 spin echo measurements of two families of surveillance return samples are shown in figure 4. In general, only small differences in the relaxation times were detected in the surveillance return (SR) samples. No direct correlation between age and relaxation time was detected, mirroring solvent swelling results. Samples in the 50X sample series were all characterized by a T_{2s} longer than found for a pristine sample of S5455. Interpreting these results in light of empirical relationships between cross-link density and relaxation times determined in our previous NMR/swelling investigations [6], this difference is consistent with higher cross-link density in the pristine sample due to manufacturing irregularities, disruption of the interfacial bonding, or effects of chain scission.

The results of T_2 measurements of the M9760 foam at ambient and 0% relative humidities are shown in figure 5. Dehydration over P_2O_5 caused a dramatic decrease in T_{2s} and an increase in T_{2L} . The differences suggest that the cross-link density has increased and the mobility of the free chains has

materials properties of the silica filled foams is an area that should be considered for further investigation. It is our belief that detailed structural and dynamic insight into the effect of water diffusion and outgassing can be obtained with NMR experiments designed with parameters determined by Thermal Programmed Desorption (TPD) of the polymer/filler matrix.

Conclusions

We have measured changes in cross-link density and average molecular weight for a series of γ -irradiated silica filled siloxane polymers by solid state NMR relaxation times. ^1H transverse relaxation times, T_2 , have been shown to be sensitive probes of changes in slow, cooperative motions occurring in the siloxane chain dynamics as a consequence of the γ -irradiation. Preliminary studies suggest that the transverse relaxation time is linearly dependent on the cross-link density in these filled PDMS systems, in agreement with previous work on unfilled PDMS systems [2,3]. For samples irradiated in air, siloxane polymer cross-linking was observed to be preceded by an initial disruption of the hydrogen bond interaction between the polymer backbone and the silica silanol groups at the interface. Stiffening due to radiation induced cross-linking then dominates the polymer chain motions at dosages above 10Mrad. Samples irradiated in vacuum undergo increases in polymer cross-linking only, with no apparent relaxation in the silica-polymer interaction. The work reported here shows that detailed characterization of the relaxation processes of the various nuclei in the siloxane polymers under static conditions has the potential to provide insight into changes in the mechanisms and energetics of motional processes brought about by polymer aging processes.

Acknowledgements

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References

- (1) Mehring, *High Resolution NMR in Solids*, Springer, 1985.
- (2) Charlesby, A., Folland, R., *Radiat. Phys. Chem.* **1980**, *115*, 393.
- (3) Cohen-Addad, J. P., Viallat, A., Huchot, P. *Macromolecules*, **1987**, *20*, 22146.
- (4) Sotta, P., Fulbur, C., Demco, D. E., Blumich, B., Spiess, H. W., *Macromol.* **1996**, *29*, 6222.
- (5) Kimmich, R., Fischer, E., Callaghan, P., Fatkullin, N., *J. Mag. Res. A* **1995**, *117*, 53.
- (6) Chien, A., Maxwell, R.S., Chambers, D., Balazs, G.B., LeMay, J., *Rad. Phys. Chem.* **2000**, submitted.